

Primary Polymer Aging Processes Identified from Weapon Headspace Chemicals

D. M. Chambers, J. M. Bazan, J. G. Ithaca

This article was submitted to
24th Aging, Compatibility and Stockpile Stewardship Conference,
Amarillo, Texas, April 30-May 2, 2002

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

March 25, 2002

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

Primary Polymer Aging Processes Identified from Weapon Headspace Chemicals

David M. Chambers and Jeanne M. Bazan, Lawrence Livermore National Laboratory,
Livermore, CA 94551

Jerry G. Ithaca, BWXT, Pantex, TX 79120

Introduction

A current focus of our weapon headspace sampling work is the interpretation of the volatile chemical signatures that we are collecting. To help validate our interpretation we have been developing a laboratory-based material aging capability to simulate material decomposition chemistries identified. Key to establishing this capability has been the development of an automated approach to process, analyze, and quantify arrays of material combinations as a function of time and temperature. Our initial approach involves monitoring the formation and migration of volatile compounds produced when a material decomposes. This approach is advantageous in that it is nondestructive and provides a direct comparison with our weapon headspace surveillance initiative. Nevertheless, this approach requires us to identify volatile material residue and decomposition byproducts that are not typically monitored and reported in material aging studies.

Similar to our weapon monitoring method, our principle laboratory-based method involves static headspace collection by solid phase microextraction (SPME) followed by gas chromatography/mass spectrometry (GC/MS). SPME is a sorbent collection technique that is ideally suited for preconcentration and delivery of trace gas-phase compounds for analysis by GC.¹ When combined with MS, detection limits are routinely in the low- and sub-ppb ranges, even for semivolatile and polar compounds. To automate this process we incorporated a robotic sample processor configured for SPME collection. The completed system will thermally process, sample, and analyze a material sample. Quantification of the instrument response is another process that has been integrated into the system. The current system screens low-milligram quantities of material for the formation or outgas of small compounds as initial indicators of chemical decomposition.

This emerging capability offers us a new approach to identify and non-intrusively monitor decomposition mechanisms that are accelerated by stockpile-relevant aging parameters such as heat, irradiation, material incompatibility and physical force. The primary organic material groups that make up many of the weapon systems are chlorofluoropolymers, polysiloxanes, and polyurethanes (PUR). In the weapon headspace we see the greatest residue from polysiloxanes and PUR and, therefore, are interested in identifying and quantifying the origin responsible for their presence. Although we have produced a number of significant findings concerning the chlorofluoropolymer and polysiloxane materials, this work focuses on the decomposition of PUR.

Experimental

Instrumentation

The system developed for this work, which is shown in **Fig. 1**, combines an Agilent GC/MS (model 6890/5973N) for sample analysis, a CTC Analytics robot (model CombiPal)

¹ Pawliszyn, J. "Solid Phase Microextraction Theory and Practice," Wiley, New York, 1987.

configured for SPME for sample processing and collection, and a Kin-Tek gas standards generator (GSG) (model 585) for response calibration. The system response is calibrated with output from the GSG, which is fed directly into a syringe wash station that was converted into a gas flow cell for the SPME fiber. Adjusting the dilution-gas flow rate to the GSG varies the concentration of the standard. For automated control of the GSG, we incorporated a DXL digital mass flow controller (model M10). Software was developed to integrate control of the GC/MS, robot, and GSG. As a result samples can be thermally processed, analyzed, and quantified automatically. Those samples not processed using the system described above were analyzed manually using this or a similar GC/MS system.

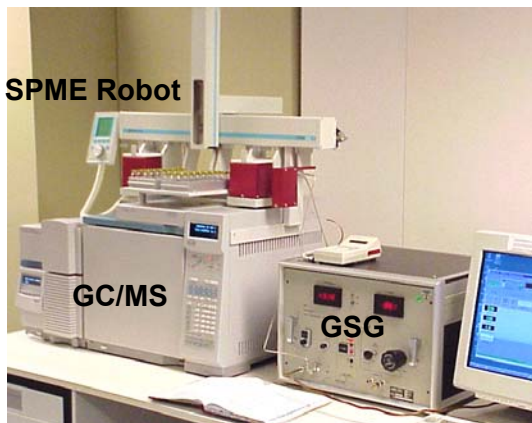


Figure 1. Photograph of automated compatibility analysis systems that incorporates an Agilent GC/MS, CTC Analytics robotic processor, and a Kin-Tek gas standards generator.

Sample Preparation and Collection

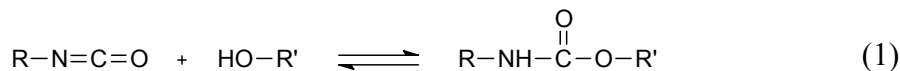
Material samples analyzed using the automated process analyzer were prepared in standard 6-ml headspace vials ranging in quantity from 10 to 500 mg under ambient conditions (approximately 35% relative humidity and 22°C). Materials processed under inert background gas environments were sealed in 50-ml flame-sealed glass ampoules. Samples were prepared at different temperatures ranging from ambient to 200°C over different periods of time. Following incubation, a SPME fiber was exposed to the sample headspace for times ranging from 20 to 60 min and analyzed by GC/MS. Permanent gases and highly volatile compounds were typically collected using an 85- μ m Carboxen-coated fiber at temperatures below 50°C and mid-range volatile compounds were typically collected with a 65- μ m DVB/PDMS-coated fiber at temperatures between 50 and 75°C. For experiments that required low-temperature collection and short collection times, we used a 100- μ m PDMS-coated fiber. These analyses were performed either on an Agilent 30 m x 0.25 mm GasPro, 60 m x 0.25 mm x 1.4 μ m DB-624, or 30 m x 0.25 mm i.d. x 0.25 μ m film HP-5MS column.

Traditional liquid-extraction analyses were performed to screen for nonvolatile polar compounds. These samples were analyzed using an Agilent 30 m x 0.25 mm i.d. x 0.25 μ m film DB-1701MS polar stationary phase.

Discussion

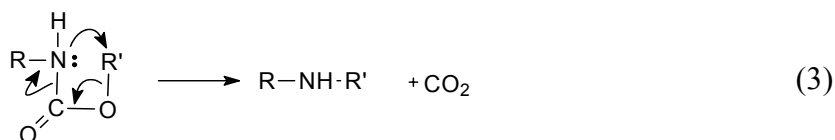
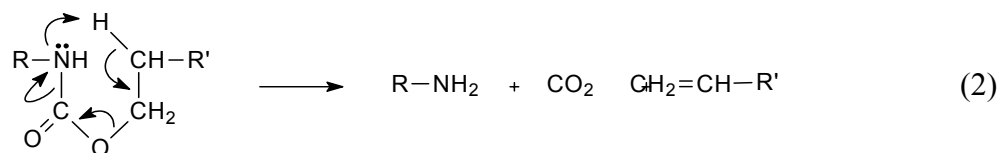
Quite often the primary decomposition mechanism for a polymer is the reverse of its synthesis, resulting in the formation of decomposition products that are the same as synthesis precursors. We found this to be the case for polysiloxanes and PUR. For this reason knowledge of the synthesis route is helpful. In the case of the PUR, the most

common synthesis approach involves the addition reaction of an alcohol to an isocyanate group.



This approach includes the 2,4-toluene diisocyanate (TDI)/polyether or polyester-based systems (e.g., TDI and PAPI) and the 4,4'-diphenylmethanediisocyanate (MDI)/polyether or polyester-based systems (e.g., Halthanes, Estanes).

The depolymerization reaction, which results in the formation of isocyanates and alcohols, is generally reported to occur at temperatures above 200°C. From our thermally accelerated material decomposition studies, we see evidence of urethane decomposition at temperatures between 150 and 200°C under both air and dry N₂ conditions. Although we do not directly monitor the urethane chain scission, we are able to detect, as shown in **Fig. 2**, the more volatile crosslinking agents (e.g., butanediol) and carbon dioxide (CO₂) from alternative decomposition routes shown below.



Although these high-temperature conditions are likely never to be experienced by the weapon materials, we have found evidence that these reactions can be driven at lower temperatures by chemical attack.

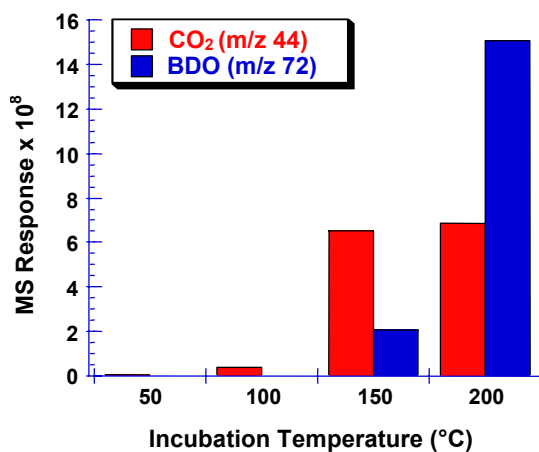
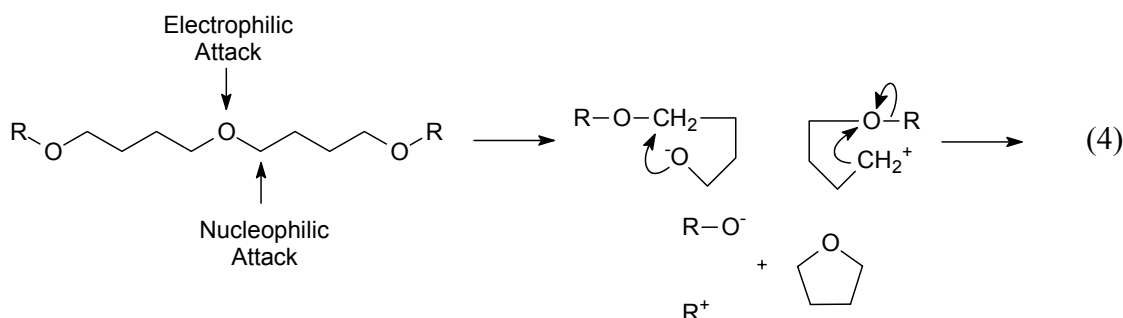


Figure 2. Volatile hard-segment decomposition byproducts produced at 50, 100, 150, and 200°C from Halthane 73-18, a polyether PUR. These byproducts are produced from decomposition of the urethane segment, which generally only occurs under high temperature or harsh chemical conditions.

At temperatures below 100°C, we observe primarily soft-segment decomposition. This is demonstrated for the Halthane PURs, which are polyether-based PURs. A major volatile byproduct seen from these materials at low temperature is tetrahydrofuran (THF), which is shown in **Fig. 3**, for samples heated at either 50, 100, 150 or 200°C for two weeks under a dry N₂ background. Although we have yet to find a supporting study on low-temperature decomposition products for polyether PUR, THF along with CO₂ have been reported as high-temperature byproducts from an MDI/1,4-butanediol (BDO) PUR.² In this work, researchers suggest that THF and water are formed at high temperatures upon the dehydration of BDO. Because we do not detect BDO or water at low temperatures (only at high temperatures as was shown in **Fig 2**), we believe THF is formed via a backbiting mechanism shown below.



We believe this reaction can be driven at low temperature by chemical attack of concomitant residue or polymer side groups. We suspect that the glycol oxygen would be susceptible to electrophilic attack and the α carbons to nucleophilic attack. Furthermore, we support a nonradical decomposition pathway because the radical dissociation energy of a carbon-oxygen single bond is approximately 320 kJ mol⁻¹. Activation energy for a chemical decomposition route is expected to be at least five times lower.³

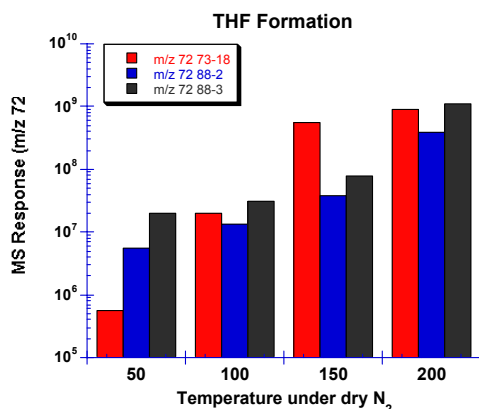


Figure 3. THF response obtained from Halthane 73-18, 88-2 and 88-3 heated under dry N₂ at either 50, 100, 150, and 200°C. We believe that the THF soft-segment decomposition mechanism is accelerated by chemical interaction at low temperatures.

²Grassie, N.; Zulfikar, M.; Guy, M.I. *J. Polym. Sci. Polym. Chem. Ed.* **1980**, 18, 265.

³Tago, K.; Tsuchiya, M.; Gondo, Y.; Ishimaru, K.; Kojima, T. *J. Appl. Polym. Sci.* **2000**, 77, 1538.

Conclusion

Of the different weapon material aging processes, we are finding that material incompatibility chemistry accelerates decomposition faster than exposure to stockpile-relevant heat or irradiation. Although the potential for decomposition at material interfaces exists, we believe that for the bulk of the materials, which are not in direct contact with other materials, decomposition is driven primarily by the migration of reactive volatile and semivolatile compounds. As a result, we define material incompatibility as the interaction of a material's functional groups (or reactive sites) with itself, an already present residue, or an outside penetrant. Furthermore, these interactions can be controlled by any condition that changes molecular mobility such as heat, weak bonding interactions, and physical force. Highly reactive compounds are the most challenging to directly monitor because they are difficult to collect and analyze as intact compounds. In some instances the decomposition routes are unknown because we are unsure of the initiating chemical responsible for accelerating a decomposition reaction. We believe this is the case for a number of materials used in weapon primary assemblies, in which we find evidence of decomposition normally seen at temperatures much higher than experienced in stockpile.

For the PUR materials evaluated in this study, we observe that at low temperatures under inert conditions the polyether PUR undergoes degradation mainly in the soft-segment region producing THF. We believe that THF is formed via a backbiting route as shown in **Eq. (4)** that is initiated by chemical attack of either oxygen or neighboring carbons.

At higher temperatures of 150°C and 200°C, we see an increase in soft-segment decomposition byproducts resulting in the formation of exponentially higher levels of THF and of larger polytetramethylene glycol fragments. The more reactive soft-segment byproducts decrease in response. In addition, hard-segment decomposition byproducts become prominent. The primary volatile byproducts we believe are associated with the hard-segment decomposition include CO₂ and BDO. These species are likely formed via mechanisms shown in **Eq. (1)**, **(2)**, and **(3)**. Although these high-temperature conditions are likely never to be experienced by the weapon materials, we have found evidence that these reactions can be driven by chemical attack at lower temperatures.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.